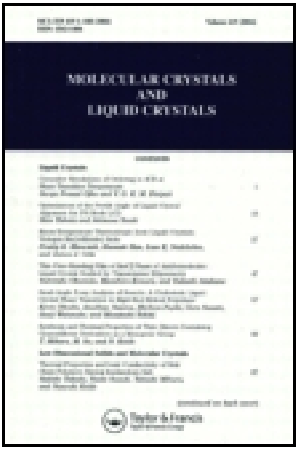

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Surface Coverage of Self-Assembed Zirconium Perylene Phosphonate Derivative Films on Quartz and Crystal Growth of Zirconium Perylene Phosphonate Derivative

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Surface Coverage of Self-Assembed Zirconium Perylene Phosphonate Derivative Films on Quartz and Crystal Growth of Zirconium Perylene Phosphonate Derivative

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The N,N'-bis(benzyl phosphonic acid)-3,4,9,10-perylene (dicarboximide) (BPPI) has been known as a photoconducting material in xerography and its layer-by-layer growth with Zr^{4+} ion as a self-assembled multilayer film has been studied. We describe a method for measuring the relative surface coverage of self-assembled zirconium-BPPI monolayer on quartz substrate using UV-Vis spectrophotometry. The crystalline Zr-BPPI was grown at the controlled pH and temperature and its morphology was flat-flake shape.

Keywords: self-assembled film; surface coverage; crystal growth

INTRODUCTION

The dyes derived from 3,4,9,10-perylenetetracarboxylic dianhydride have been known for several decades as the dyes possessing excellent light fastness. But only recently has it been recognized that the dyes are photochemically stable and the fluorescence quantum yields are high[1]. In the previous paper[2],we already reported the layer-by-layer growth of the self-assembled Zr-BPPI multilayer film on silicon surface. In this paper, we report the surface coverage of self-assembled Zr-BPPI films on quartz plate and the growth of crystalline Zr-BPPI powder in the solution. Figure 1 shows the structure of BPPI molecule.

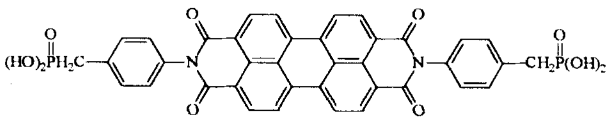


FIGURE 1 The structure of BPPI

EXPERIMENTAL

The structure of Zr-BPPI monolayer is most stable at pH 6-7, but this structure will be destroyed at over pH 10. Therefore, the degree of crystallization is increased in low pH region. These facts enable us to calculate the surface density of the BPPI on the Zr-BPPI monolayer[3]. The polycrystal of Zr-BPPI was synthesized by controlling pH with HCl and KOH. The Zr-BPPI precipitates were formed as soon as mixing the solutions of $ZrOCl_2$ and BPPI at pH 4.33. To increase crystallinity, the BPPI solution was added to $ZrOCl_2$ solution very slowly (BPPI : $ZrOCl_2$ 1:1 by volume) and then the control of pH was needed. The appropriate condition of pH was 4.33. The Zr-BPPI solution was kept at room temperature for crystal growth for 2 months.

RESULTS AND DISCUSSION

As shown in Figure 2(a), the maximum absorbance was observed at 465 nm with the relative intensity of 0.013 from the visible spectrum of the Zr-BPPI monolayer that was exfoliated from the substrate in 10 mL of KOH aqueous solution. The independently measured extinction coefficient was calculated from a plot of several concentrations vs absorbance of the KOH aqueous solution that contains Zr-BPPI crystal at 465 nm (A_{soln}). Figure 2(b) shows the UV-vis spectrum of powder crystalline Zr-BPPI in KOH aqueous solution at different concentrations. The extinction coefficient from this plot (ε_{soln}) was determined to be 2.3235×10^4. The concentration of Zr-BPPI on the quartz calculated from these values is 5.724×10^{-9} mol. The calculated absolute density was determined from the following equation.

$$\text{Surface density} = (C\times 6.02\times 10^{23}/\text{mol})/(\text{surface area}) = 5.76/100\ \text{Å}^2$$

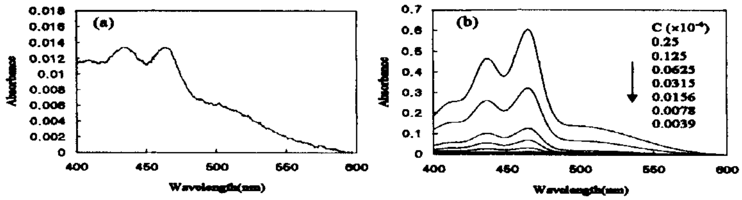
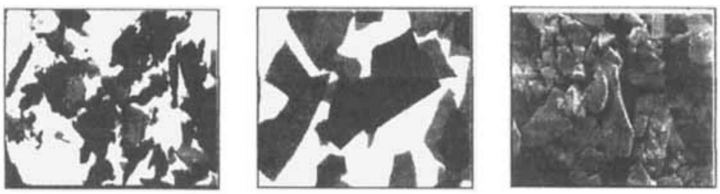


FIGURE 2 (a) UV-vis spectrum of Zr-BPPI exfoliated from Zr-BPPI monolayer. (b) UV-vis spectra of powder crystalline Zr-BPPI solution in KOH aqueous solution at different concentrations.

The calculated value is rather high compared to the value of monolayer density (about less than 4/100 Å ^{2})[3], probably because of physisorbed BPPI molecules on the top of monolayer surface.The stability and degree of long-range order of Zr-BPPI multilayer films is likely to be dependent strongly on the identity of the metal ion and the structure of the corresponding bulk metal phosphonate phase. Therefore, we investigated the morphology of Zr-BPPI powders. Figure 3(a) shows the Zr-BPPI precipitates formed immediately after mixing Zr^{4+} and BPPI solutions. Figure 3(b) and (c) show the polycrystalline Zr-BPPI powders after aging for two months. Zr-BPPI precipitates show irregular shape of powders, but Zr-BPPI polycrystals show a flat-flake shape. It is strongly supported that the flat shaped Zr-BPPI crystals grow well at the controlled pH condition. The size of Zr-BPPI crystals are 20 ~ 100 ㎛ and the thickness of crystals is about 10 ㎛



(a) (× 500) (b) (× 500) (c)

FIGURE 3 (a) Optical microscopic image of Zr-BPPI precipitates. (b) Optical microscopic image of Zr-BPPI crystal. (c) SEM image of crystalline Zr-BPPI

CONCLUSION

The surface coverage of Zr-BPPI monolayer is 5.46 BPPI molecules per 100 $Å^2$ on the silicon substrate. The crystalline Zr-BPPI was grown at the controlled pH and temperature and its morphology was flat-flake shape.

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References

[1] A. Rademacher, S. Markle and H. Langhals, *Chem. Ber.*, **115,** 2927 (1982).
[2] H. J. Chae, Y. Kim, H. Lee, *Bull. Chem. Soc. Kor.*, **19,** 27(1998).
[3] J. H. Moon, J. W. Shin and J. W. Park, *Langmuir*, **12,** 4621 (1996).